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PAPERS READ BEFORE THE ACADEMY.

I.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF BARIUM.

FIRST PAPER: THE ANALYSIS OF BARIC BROMIDE.

BY THEODORE WILLIAM RICHARDS.

Presented January 11, 1893.

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INTRODUCTION.

In the course of a recent determination of the atomic weight of copper,* there was an attempt made to determine the ratio of cupric to baric sulphate; but in the discussion of the result it became evident that the ordinary method of precipitation was far too crude for the desired purpose. Moreover, even had there not been possible errors of a serious nature in the method, the atomic weight of barium was evidently too uncertain to form the basis of any accurate comparison. Hence this attempt was at the time given up, and the plausibility of the single result obtained was ascribed to a chance elimination of opposite errors.

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* These Proceedings, Vol. XXVI. p. 258.

During the early part of this century, a number of chemists have investigated the atomic weight of barium with very widely varying results. The first experiments worthy of mention were made by Berzelius and Klaproth;[*] but these are now of historical interest only. In 1818 the problem was again undertaken by Berzelius,[†] who found that from 100.00 parts of anhydrous baric chloride he could obtain 138.07 parts of argentic chloride; whence the atomic weight is readily computed to be 136.8. At the same time he found that the same amount of baric chloride yielded 112.175 parts of baric sulphate, which gives Ba = 135.6.

In 1829 Edward Turner[‡] published a redetermination of the latter ratio, finding the equivalents to be as 100.00 : 112.19. He too weighed the argentic chloride obtainable from a given amount of baric chloride, and arrived at the conclusion that the atomic weight of barium could not be far from 137.45. Two years later T. Thomson[§] described several attempts to weigh barium as the sulphate, which need not be further discussed. In 1833 Turner[‖] found as a mean of three experiments that 112.03 parts of baric nitrate were required to form 100.00 parts of baric sulphate; a result indicating 137.0 as the atomic weight of barium. Ten years later Salvetat[¶] published a very incomplete account of the quantitative study of the conversion of baric carbonate into sulphate, giving a final result of 136.

Soon after this both Pelouze[**] and Marignac[††] determined the ratio of baric chloride to metallic silver, the first finding the atomic weight of barium to be 137.3, and the second 137.1. In 1850 Levol[‡‡] reduced auric chloride with sulphurous anhydride, and determined the sulphuric acid which resulted with baric chloride. Recalculated with the recently determined atomic weight of gold, 197.3,[§§] these results give 138.3 as the atomic weight of barium.

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[*] See Wollaston, Phil. Trans., 1814, p. 20.

[†] Pogg. Annalen, VIII. 189.

[‡] Phil. Transactions, 1829, p. 296.

[§] System of Chemistry, 7th Edition, 1831, I. 426.

[‖] Phil. Transactions, 1833, p. 538.

[¶] Compt. Rend., XVII. 318.

[**] Ibid., XX. 1047.

[††] Liebig's Annalen, 1848, LXVIII. 215.

[‡‡] Ann. Chim. Phys., [3.] XXX. 359.

[§§] Krüss, 1887; Thorpe and Laurie, 1887; and Mallet, 1889.

In the next year H. Struve[*] found that 100 parts of baric chloride produced 112.094 parts of baric sulphate, a value which leads to an atomic weight of barium equal to 137.0. T. Andrews[†] obtained in 1852 the value 137.6, but he gives none of his details. Six years afterwards Marignac[‡] redetermined the ratio of baric chloride to the sulphate, with a result very different from those of his predecessors. In his hands one hundred parts of the former salt yielded only 112.011 parts of the latter, instead of 112.09 or more. In the same investigation he determined the amount of water of crystallization in baric chloride, with results so unsatisfactory that the values calculated from the various ratios varied from 128.5 to over 138,[§] as well as the ratio of baric chloride to metallic silver. This last determination led to a value for barium only four one-hundredths of a unit higher than his previous work, ten years before. He admits that the substances used in the analysis were not perfectly pure, but assumes that the impurities were not great enough seriously to influence the result. At about the same time Dumas[||] was also determining the ratio of baric chloride to silver. He fused the salt in a stream of hydrochloric acid gas, but gives no proof that a slight excess of the gas was not absorbed. If this had been the case, of course the observed atomic weight of barium would have been too low. As a matter of fact, he obtained 137.0 for the value of this "apparently variable constant." Below is tabulated a list of the various determinations, grouped according to the processes employed.

The Atomic Weight of Barium.[¶]

O = 16.000.

Analysis of Baric Carbonate:	
Berzelius, 1811	Ba = 134 to 143
Wollaston and Klaproth, 1814	139.2
Salvetat, 1843	136

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[*] Liebig's Annalen, 1851, LXXX. 204.

[†] Brit. Assoc. Report, 1852, Part 2, p. 33.

[‡] Liebig's Annalen, CVI. 165.

[§] See Meyer and Seubert's "Atomgewichte," p. 176.

[||] Liebig's Annalen, CXIII. 22.

[¶] The writer is much indebted to the works of Becker, Clarke, Meyer and Seubert, and Ostwald for valuable assistance in preparing this list.

Conversion of Baric Chloride to Sulphate:	
Berzelius, 1818	Ba = 135.6
Turner, 1829	Ba = 135.4
Thomson, 1831	Ba = 136±
Struve, 1851	Ba = 137.0
Marignac, 1858	Ba = 138.5
Conversion of Nitrate into Sulphate:	
Turner, 1833	Ba = 137.0
Comparison of Baric Sulphate with Gold:	
Levol, 1850	138.3
Ratio of Baric Chloride to Argentic Chloride:	
Thomson	Ba = 136±
Berzelius, 1818	Ba = 136.8
Turner, 1829	Ba = 137.4
Marignac, 1858	Ba = 137.1
Ratio of Baric Chloride to Silver:	
Pelouze, 1845	137.28
Marignac, 1848	137.11
Marignac, 1858	137.15
Dumas, 1859	137.00
Ratios including Water of Crystallization:	
Marignac, 1858 (averages)	130.7 to 138.5
Unknown Ratio:	
Andrews, 1852	137.6
Clarke, 1883, selects*	Ba = 137.0
L. Meyer and Seubert, 1883, select	Ba = 137.2
Ostwald, 1885, selects	Ba = 137.04
Van der Plaats, 1886, selects	Ba = 137.1

A cursory glance at the list will show a lamentable lack of consistency in the results of even a single method in different hands. The only ratio which seemed capable of yielding approximate results was the ratio of baric chloride to metallic silver, and here the variations in the atomic weight of barium amounted to nearly three tenths of a unit. The question whether the errors were due to mechanical defects of analysis, or to admixture of foreign substances, became an important subject for consideration; but it is evidently of little use to recalculate such heterogeneous results. The necessity for a careful experimental revision is very apparent. Such a revision would be especially interesting in view of the fact that barium is a member of one of the best marked series of elements known, — a series which might yield important information regarding a possible mathematical relation of the atomic weights. Moreover, the atomic weights of no less than eighteen other elements[*] have been determined, at one time or another, by reference to baric sulphate. Most of these determinations have been made without the least precaution with regard to the baric chloride occluded in the precipitated sulphate, or on account of the solubility of the sulphate itself; but even if the method had been satisfactory, the determinations could not be considered as anything more than crude approximations, because of our uncertainty regarding the molecular weight of baric sulphate.

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* In Clarke's original treatise 137.007 is apparently misprinted for 137.07 (Smithsonian Misc. Coll., Vol. XXVII. p. 63).

These were some of the considerations which prompted the present undertaking. It is not unnatural that the revision should have been begun with the more or less strong belief that the atomic weight of barium could not be far from 137.1; but the progress of the work has completely overthrown this belief, and has indicated a much higher value.

Balance and Weights.

The balance and weights were identical with those used in the latter part of the investigation upon copper,[†] hence a further description of them is unnecessary. The weights were gently and carefully rubbed, and again standardized with reference to each other; a proceeding which yielded values essentially identical with the two previous standardizations. The first ten-gramme weight was also compared from time to time with the platinum weight which had been carefully standardized in Washington,[†] in order to test its constancy.

		True Grammes.
Oct. 18, 1891	Ten-gramme weight	= 10.00023
May 16, 1892	" "	= 10.00023
Nov. 1, 1892	" "	= 10.00022
Nov. 2, 1892	" "	= 10.00020

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[*] Li, Be, F, Mg, Si, V, Cr, Ni, Cu, Se, Y, In, (Ba), La, Ce, Di, Au, Tl, Th. Compare L. Meyer and Seubert's "Atomgewichte," p. 165.

[†] These Proceedings, XXVI. 242.

The second ten-gramme weight, which was much less used, remained quite constant in value.

Throughout the present investigation the method of weighing by tares was universally adopted. A vessel to be weighed was placed upon the left hand scale pan, balanced with common gilded weights, and then replaced by a similar vessel which weighed a few milligrammes less. The exact amount of this extra tare having been determined with the rider, the counterpoise was replaced by the original vessel and the rider removed, in order to determine if the centre point had changed. When only a slight change had taken place, the reading for the counterpoise was compared with the mean of the two readings for the original vessel. In the rare cases when the change exceeded the equivalent of the thirtieth of a milligramme, the vessels were alternately substituted for each other until constancy was reached. A substance to be weighed was of course placed in such a tared vessel, and after substitution the deficiency of the counterpoise was made up with standard weights. The difference between the tares on the left hand scale pan indicated the observed weight in air of the substance taken. It was found convenient to tabulate the results in the following form.

	Common Weights: Right hand pan. Grammes.	Tare: Standard Weights. Left hand pan. Grammes.	Cor. to Standard Weights. Milligrammes.	Corrected Standard Weights. Grammes.	Correction to Vacuum. Milligrammes.	True Weight of Substance taken. Grammes.
Weight of crucible + substance	22.0890	1.80986	—0.05	1.80981		
Weight of crucible alone	20.2797	0.00081	0.00	0.00081		
Weight of substance, cryst. baric bromide	1.8093	1.80905		1.80900	+0.30	1.80930

The lowest right hand figure represents the true weight of the substance taken, if the Sartorius ten-gramme weight is taken as the standard. Reduced to the Washington standard the value becomes 1.80934; but this last correction is in no case applied in the work which follows.

The method used in the case of hygroscopic substances, and most other precautions, are given at length in the paper already quoted. In weighing a crystallized salt it was usually necessary to weigh the crucible while filled with ordinary moist air, hence the counterpoise crucible was exposed to the same conditions.

During the latter part of the investigation the balance was kept in a small room built entirely inside of the main laboratory. The absence of outside windows in the small room caused a notable absence of air currents and rapid changes of temperature, while its glass walls supplied plenty of light.

It is almost needless to state that, while the weights of the apparatus were not reduced to the vacuum standard, — on account of the method of weighing, which rendered such reduction unnecessary, — the weight of every substance used was corrected in the manner shown above for the difference between the weight of air displaced by it and that displaced by the corresponding brass weights. Where the specific gravity of the substance was not already accurately known, it was carefully determined for this purpose.

The Spectroscopic Detection of Calcium and Strontium in the Presence of Barium.

In the course of the search for a typical barium salt it became important to determine how small an amount of calcium and strontium could be detected in the presence of large amounts of barium. The most sensitive method is naturally the spectroscopic one, but no literature giving the degree of sensibility seemed to be at hand.

The first phase of the problem to be investigated was the determination of the amount of calcium and strontium which could be detected in the absence of barium. Hence a standard solution of calcium and strontium was prepared containing 0.8 milligramme of each metal to the cubic centimetre. This solution was successively diluted and tested by means of a well made single prism spectroscope with an adjustable slit. A drop of the solution was supported upan a coil of wire containing 0.018 cubic centimetre, similar to that suggested by Truchot * and so ably used by Gooch and Hart.† No attempt at quantitative analysis was made, the present problem being merely the determination of the limit of visibility.

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* Compt. Rend., LXXVIII. 1022.

† Am. Journ. of Sci., [3.] XLII. 448. **The writer is much indebted to this paper for valuable hints.**

RESULTS.

Dilution.	Weight of Ca. and Sr. vaporized.	Observations.
Solution : Water.	Milligrammes.	
1 : 0	0.014	Brilliant.
1 : 5	0.003	"
1 : 10	0.0014	Very plainly visible.
1 : 20	0.0007	" " "
1 : 40	0.0004	Plainly visible.
1 : 100	0.00014	Both visible.
1 : 200	0.00007	Both scarcely visible.
1 : 400	0.00004	Both invisible.

Hence seven hundred-thousandths of a milligramme is about the limit of visibility under these conditions. It is remarkable that this result should be essentially identical with Bunsen's result obtained by a different method.*

It has long been known† that the best method for detecting small quantities of strontium and calcium in the presence of barium is to evaporate the solution of the chlorides to small bulk, precipitate most of the baric chloride by means of alcohol, and test the filtrate. From this filtrate, by means of two or three repetitions of the fractionation with alcohol, it is possible to eliminate nearly all the barium. It is evident, on the other hand, that if the precipitate is dissolved and reprecipitated several times, all the calcium and strontium must go into the mother liquors. This is one of the most rapid methods of obtaining pure baric chloride; it served for the preparation of the material used in the succeeding experiments.

In the first experiment half a milligramme of calcium was added to the solution of three grammes of very pure baric chloride. Upon the usual fractional treatment a most brilliant calcium spectrum was obtained from the mother liquor. One fifth of a milligramme of calcium in another experiment gave similar results. For a third experiment one fiftieth of a milligramme each of calcium and strontium was added to five grammes of crystallized baric chloride. The mother liquor from the first precipation by alcohol was evaporated to dryness and extracted with alcohol. Calcium was very evident in the extract, but no trace of strontium. The reason for the apparent absence of the latter metal is to be found in the fact that the mother liquor was evaporated to dryness. To prove this, the same amount of materials were fractionally precipitated three times, and a very evident strontium spectrum was given by the last mother liquor. In the fifth trial, only one two-hundredth of a milligramme of strontium was used. Upon three fractionations no strontium could be detected; but upon dissolving and reprecipitating each of the precipitates once more a faint test for the metal was found in the final mother liquor. This is evidently about the limit so far as strontium is concerned. Calcium may be detected when it is present in quantities much less than the two-hundredth of a milligramme, because of the ready solubility of its chloride in alcohol. The baric chloride used gave no trace of the calcium or strontium lines after most careful fractionation.*

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* Compare Vogel's "Spectralanalyse irdischer Stoffe," 1877, pp. 92, 94.

† Ibid., p. 99.

From these experiments it may be concluded that, when a baric salt shows no trace of the allied metals upon the treatment just described, it does not contain a weighable amount of them. Nevertheless, in the work which follows, the purification was usually continued long after the visible traces of strontium and calcium had been eliminated.

The Choice of Material.

It has been already stated that the most satisfactory determinations of the atomic weight of barium have had baric chloride as a starting point. In many respects this substance is well adapted for the purpose; but one serious cause of error must be carefully guarded against in the usual method adopted for its analysis. The well known solubility of argentic chloride influences the accuracy not only of the weight of chloride obtained, but also of the apparent end point of the precipitation after the method of Gay Lussac. Long ago Stas † pointed out this cause of error, and carefully described his method of procedure, that others might correct his results if they were found to be based upon an incorrect assumption. He added an excess of silver to the chloride to be investigated, and then added the standard solution of a chloride until no more cloudiness was observable. Such a method under ordinary circumstances requires from two to eight milligrammes less of silver to correspond with a given weight of chloride than would be required if the solutions were added in the inverse order.

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* A trace of sodium was always found in even the purest specimens. It is probable that this trace was derived from the air during the course of fractional treatment necessary to eliminate the barium.

† Aronstein's translation of Stas's Memoir, pp. 46, 56, 59, and especially 295 (Leipzig, 1867).

A number of years afterward * Stas changed his method of procedure, and selected the point half-way between the two extremes as the true end point of the silver reaction. He gave reasons for this change of view, but wholly ignored his previous results. Commentators have laid hardly enough stress upon this important difference between the two series of determinations, although it necessarily involves an error in one series or the other.

Working before even the earliest date of Stas's publication upon this subject, the experimenters upon the atomic weight of barium naturally overlooked the whole question. As nearly as may be guessed from their incomplete accounts, they usually selected the end point obtained by gradually adding argentic nitrate to baric chloride; hence their results cannot be compared with either of Stas's series.

Much time during the past eighteen months has been spent upon this question. The investigation of baric chloride showed that results for the atomic weight of barium varying from 137.35 to 137.50 might easily be obtained from the purest possible salt, according to the interpretation of the data. At last a definite conclusion was reached, and the work is now nearly ready for publication.

The necessity for some other basis for the atomic weight of barium early led to the search for a new starting point. In the course of this search, most of the available baric salts were investigated with regard to their adaptability for the present purpose.

Baric nitrate holds water with great obstinacy, and no certain point of constant weight could be reached by gradually heating it. Besides, the only two methods available for its analysis are extremely unsatisfactory. The conversion into the chloride is rendered very difficult because of the insolubility of both the nitrate and chloride in strong acids. The complete conversion of the

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* The Memoir was presented in 1876, according to the title page. Mém. de l'Acad. de Belg., Nouv. Sér., XLIII. See also Van der Plaats, Chem. News, LIV. 52, 88.

nitrate into the sulphate is also difficult because of the well known occlusion of one salt by the other. Moreover, supposing the analysis by either method to have been satisfactorily performed, the data furnished would give only the worst possible foundation for the calculation of the atomic weight of barium.* Many qualitative and quantitative experiments led to the complete rejection of baric nitrate as the material for analysis.

Baric bromate is very readily prepared in a pure state by a few successive crystallizations, and it was hoped that this salt would furnish especially valuable testimony upon the case. But investigation showed that it was impossible to be certain that the crystallized salt did not contain an excess of occluded water. Upon the other hand, it is doubtful if all the water of crystallization can be expelled without a slight decomposition of the salt. Since water is the one impurity most to be dreaded in all such work, baric bromate was rejected, except as a means of obtaining the bromide in a pure state.

The carbonate was next experimented upon; and while the results were more promising than those from the nitrate and bromate, they were less satisfactory and conclusive than those obtained from baric bromide.

The advantages of the use of a bromide for an investigation upon atomic weights are so manifest, and have been so often discussed, as to need no further mention. The current descriptions of the deliquescence and instability of the baric salt alone postponed the consideration of this substance. Investigation showed that misleading statements about the salt have found their way into chemical literature. In reality, the substance is as well adapted for accurate work as baric chloride and most other materials upon which we must rely.

THE PROPERTIES OF BARIC BROMIDE.

Baric bromide crystallizes from aqueous or dilute alcoholic solutions in doubly terminated monoclinic† prisms, which are somewhat hygroscopic, but not deliquescent in ordinary weather.

The crystallized salt contains two molecules of water, together with the slight excess which is usually to be found in such crystals.

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* See Ostwald, Allgemein. Chem., I. 23.

† Werther, Journal für prakt. Chem., XCI. 167. Also Von Hauer, same Journal, LXXX. 230. Rammelsberg states that the salt is isomorphous with baric chloride (Pogg. Ann., LV. 237).

Below the temperature of 70° in somewhat moist air, or at the ordinary temperature in perfectly dry air, it loses one of these molecules.* The other one is retained until a temperature of from 100° to 130° is reached, according to the hygroscopic condition of the surrounding air.

The accuracy of the final result for the atomic weight of course depends upon the complete absence of water from the dried salt; hence an especial series of experiments was made to determine the conditions under which the water was completely expelled. Upon heating to redness, the salt is very slightly decomposed; † hence in all cases where a high heat was used the amount of baric hydroxide and baric carbonate formed were determined by means of very dilute standard hydrobromic acid, using phenol phthaleïn and methyl orange respectively as the indicators. The accuracy which it is possible to attain in this process was a great surprise. If a very small amount of pure boiled water is used for the solution of the baric bromide, a deficiency of less than a tenth of a milligramme of bromine in five grammes of the salt is detected with the greatest ease. The correction applied to the weight of the baric bromide was of course always the calculated difference between the weights of the bromine and the hydroxyl, or the carbonic acid, which had taken its place. For example, a deficiency of 0.81 milligramme of hydrobromic acid found by alkalimetry involved a correction of 0.63 milligramme if the alkaline earth had been found in the form of hydroxide, or 0.50 milligramme if it had been found in the form of carbonate. Since baric carbonate is very faintly alkaline to phenol phthaleïn, this correction is not absolutely exact; but its error is an infinitesimal one so far as this work is concerned. It is probable that, if any traces of oxide were formed, they were converted into hydroxide or carbonate before the crucible cooled.

One experiment showed that 1.6 grammes of baric bromide dried at 136° lost 0.4 milligramme on being heated to dull redness. On another occasion, three grammes of baric bromide which had been dried at 200° to constant weight lost 0.50 milligramme upon heating to dull redness. Alkalimetry indicated that 0.32 milligramme should be added to the last weight as a correction for the bromine lost; hence the corrected loss was 0.00018 gramme, or 0.006 per cent. A third trial gave the corrected loss of 3.5 grammes of baric bromide between 185° and a dull red heat as 0.00027 gramme, or 0.008 per cent. Again, 3.4 grammes of a less pure specimen of the salt lost 1.2 milligrammes between 200° and dull redness, of which loss eight tenths of a milligramme was accounted for by the baric carbonate found in the dissolved residue. In Experiment 19, about 3.5 grammes of the salt dried at 260° lost 0.04 milligramme on heating to 340°, and 0.27 milligramme more upon subjection to a red heat. In order to prove that the method of desiccation over sulphuric acid was sufficient for the purpose in hand, this specimen was again heated to 400°, and cooled in a vacuum over phosphoric oxide. After the admission of dry air the crucible and contents were found to have *gained* a little less than a twentieth of a milligramme. Since seventeen one-hundredths of a milligramme must be added to the last weight of the salt to correct for the amount of alkali found, it is evident that the salt dried at 340° in the first place could not have retained more than 0.005 per cent of water, which could be expelled at a red heat.

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* 2.8688 grammes of crystallized baric bromide lost 0.1547 gramme on heating to constant weight at 70–80°; the residue lost 0.1533 gramme more upon heating to constant weight at 160°. Compare Graham Otto (Michaelis), III. 662.

2.0506 grammes of baric bromide which had been powdered and dried over sulphuric acid to constant weight lost 0.1181 gramme upon drying at 200°.

† Schultze, Jour. f. prakt. Chem., [2.] XXI. 407.

The most severe test of the hygroscopic constancy of baric bromide was obtained by fusion. 17.4841 grammes of baric bromide which had been thoroughly dried at a dull red heat were fused in a platinum crucible, and were found to have lost 4.1 milligrammes during the process. 2.25 cubic centimetres of twentieth normal hydrobromic acid were required to render the solution of the clear cake neutral to phenol phthaleïn, and 0.10 cubic centimetre more made it strongly acid to methyl orange. These figures involve a correction of 7.0 milligrammes to the second weight of baric bromide, making it 17.4870 grammes. The excess of this weight over the first (17.4841) is completely accounted for by the knowledge that a slight indeterminable correction* should have been applied to the earlier one, owing to its previous loss of bromine. The crucible was found to have lost 0.20 milligramme.

Again, two grammes and a half of baric bromide heated to constant weight at 185° lost 2.11 milligrammes on being fused in a double crucible. Of this weight all but 0.17 milligramme (0.007

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* From 0.010 to 0.03 per cent.

per cent) was accounted for by the amount of alkali found in the dissolved residue (Experiment 13). In Experiment 4, given below, the bromide was also fused. Although this sample was not weighed at any lower temperature, it is evident from the amount of silver it required that about the same relation must hold true. It is a necessary conclusion from these results that baric bromide loses no more water upon fusion than upon being heated to dull redness without fusion. This constancy of hygroscopic condition gives strong ground for the inference that the ignited salt is wholly free from water, and that the salt dried at 180° contains only about seven thousandths of one per cent of the impurity. Moreover, it is very unlikely that water and baric bromide could remain together at a red heat without mutual decomposition. The question of the absolutely anhydrous condition of most substances must necessarily be a matter of inference, because our methods for the determination of a few tenths of a milligramme of water in the presence of a large amount of other material which may be volatilized are not sufficiently accurate to furnish direct evidence upon this point. Our knowledge regarding baric bromide is hence as full as it is possible to obtain.

The specific gravity of baric bromide has been determined by Schiff.* According to his results the crystallized salt is 3.69 times heavier than the same volume of water, while the anhydrous salt is 4.23 times heavier. Since it is important in reducing weights to the vacuum standard to know the exact values of these physical constants, new determinations were made. Carefully redistilled dry toluol, in which baric bromide is insoluble, was taken as the liquid to be displaced, and two specific gravity bottles were used. The weight of water filling the first bottle was found upon three trials to be 11.4117, 11.4133, and 11.4120 grammes, these values being corrected to 4° for the expansion of the water, but not corrected for the expansion of the glass (24°) nor for the air displaced by the water and weights. An approximate determination of the coefficient of expansion of toluol gave the means of reducing all the weighings with that liquid to the same standard of 24°. Three weighings gave results for the weight of toluol filling the bottle to be 9.8357, 9.8356, and 9.8342 grammes; and 4.4262 grammes of large clear crystals of baric bromide were found to displace 1.0141 and 1.0126 grammes of toluol at 24°. Hence the specific gravity of crystallized baric bromide at 24° compared with water at 4° is 3.852. No correction is made for the difference in volume of the weights employed.

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* Liebig's Annalen, CVII. 59; also CVIII. 23.

A sample of baric bromide was dried at 200°, powdered very rapidly, transferred to the specific gravity bottle, and heated for a long time at the softening point of glass. After cooling in a desiccator the weight of the baric salt was found to be 7.6808 grammes. After filling with dry toluol, removing the atmospheric pressure, and shaking as usual, the gain in weight was 8.3878 grammes, as a mean of two closely agreeing trials. Since the volume of the pycnometer had slightly altered during the heating, the bottle was remeasured and found to contain 11.3338 grammes of water at 4° (not corrected for the expansion of the glass), and 9.7685 grammes of toluol at 24°. These data give a result for the specific gravity of anhydrous baric bromide equal to 4.794.

Since the apparatus was not perfect, a new specific gravity bottle was prepared, which gave far more concordant results. With this apparatus 5.7271 grammes of baric bromide, dried for a long time at 200°, were found to displace the same volume as 1.1979 grammes of water at 4°. Here again the salt and toluol were at 24°, and the weights were not corrected for the different volumes of the brass. These figures indicate a specific gravity of 4.781, — not very different from the previous result, but very different from the value obtained by Schiff. The value 4.79 is used in all calculations which follow.

One hundred parts of water dissolve about one hundred parts of anhydrous baric bromide at ordinary temperatures, and nearly one hundred and fifty parts at the boiling point of water.* The salt was found to be much less soluble in alcohol than one would expect from the literature on the subject.

A saturated solution in 87% alcohol contains only about six per cent of baric bromide at the ordinary temperature. In absolute alcohol the salt is even less soluble. These facts had an important bearing on the methods of purification.

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* See Graham Otto, *loc. cit.* Also recent experiments here.

Preparation of Materials.

Baric Bromide. — This substance was prepared in five distinct ways, with the intention of determining whether the salt is capable of being obtained in a perfectly typical state.

In the first place pure baric carbonate was prepared from pure baric nitrate. To make this latter substance the baric nitrate of commerce ("purissimum"), containing traces of strontium, calcium, potassium, and sodium, was recrystallized seven times from boiling water by cooling. Baric nitrate is the most convenient starting point for the preparation of a typical barium salt, since its solubility rapidly diminishes with the temperature, and is so much less than that of the calcium and strontium salts. Even after the second recrystallization the alcoholic fractionally precipitated extract of a large amount of the mother liquor, which had been evaporated with excess of pure hydrochloric acid, showed no trace of calcium or strontium bands in the spectroscope. The pure salt, which had been recrystallized seven times, was dissolved in a large platinum vessel in water which had been distilled in a platinum retort, and was treated with an excess of pure ammonia water which had also never come in contact with glass or porcelain. Into this perfectly clear solution was led a current of pure carbon dioxide, prepared by the action of pure sulphuric acid on sodic hydric carbonate. It was found impossible to free such carbonic acid from a trace of sodium, shown by conducting the gas into a lamp flame, as long as the sodic hydric carbonate was dry. After this last substance had been submerged under two inches of water, the gas evolved was easily obtained in a perfectly pure state by passing it through a sufficient number of washing bottles containing at first a weak solution of sodic hydric carbonate and finally pure water.

The pure baric carbonate was washed with hot distilled water until twenty five cubic centimetres of the wash water showed no trace of ammonia upon the addition of Nessler's reagent. The last washing was with water which had been distilled in platinum. The snow-white preparation was dried and gently ignited over a spirit lamp in a platinum dish.

From this baric carbonate three different preparations of baric bromide were made, by dissolving it in two different samples of hydrobromic acid and varying other conditions. The first sample of acid was prepared from perfectly pure bromine. This had been made by the distillation of a mixture of potassic permanganate with a dilute solution of an excess of potassic bromide and pure sulphuric acid. Before being converted into hydrobromic acid the bromine was redistilled after solution in potassic bromide and agitation with zincic oxide.* The bromine was in the first place poured into pure baric hydroxide, and, after the separation of the greater part of the baric bromate, was converted into hydrobromic acid by pure sulphuric acid. The baric hydroxide is easily freed from the usual trace of chlorine by five recrystallizations from hot water; in this case the substance was crystallized nine times. The sulphuric acid had been redistilled three times, the first and last portions being rejected.

The dilute hydrobromic acid, containing a small amount of free bromine set free by the remaining baric bromate, was distilled. The colored first portion of the distillate was thrown away, and a portion of the second fraction was analyzed to prove its purity. 1.82471 grammes (in vacuum) of silver,† dissolved with all possible care in the purest nitric acid, yielded 3.17641 grammes (in vacuum) of argentic bromide upon precipitation with a slight excess of the acid. Hence the percentage of silver in the precipitate must have been 57.446, a result which is essentially identical with Stas's result 57.445.

In this hydrobromic acid a portion of the pure baric carbonate was dissolved, and the solution was evaporated with a slight excess of baric carbonate to the point of crystallization. The crystals were dried over the water bath and ignited at a dull red heat over a Berzelius lamp for half an hour. The filtered solution was allowed to stand until neutral to phenol phthaleïn, showing that all the small amount of baric hydroxide formed upon heating had been eliminated, and after filtration was evaporated. As before, the mother liquor was rejected; the crystals were washed twice with pure redistilled alcohol and dried in the air. These crystals formed the first preparation, designated I.a, and served for the two preliminary analyses.

The second preparation of baric bromide was made from a similar specimen of baric carbonate by its solution in hydrobromic acid, prepared essentially in the manner described in the work upon the atomic weight of copper.‡ To test the purity of this acid 1.60376 grammes (in vacuum) of silver were dissolved and precipitated by a slight excess of the acid, yielding 2.79184 grammes (in vacuum) of argentic bromide. Hence the percentage of silver in the precipitate was 57.444 (according to Stas, 57.445). The baric bromide made from this acid was recrystallized, ignited at dull redness, dissolved, allowed to stand exposed to the air, filtered, crystallized, dehydrated, and fused at bright redness by means of an alcohol lamp. Finally, after solution, filtration, slight acidification with hydrobromic acid, and two successive crystallizations, the small amount of substance which remained was used for Analyses 3 and 4 (Preparation No. I.b). The salt contained in the last mother liquor was fused into an absolutely clear limpid liquid, dissolved, faintly acidified, filtered, and recrystallized, the crystals being washed with alcohol, and finally analyzed under the designation No. I.c (Analysis 5). It is needless to say that in all the concluding operations platinum vessels and the purest water alone were used.

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* Stas, Mém. Acad. Belg., N. S., XLIII., Part II, p. 38.

† See page 22 of this paper.

‡ These Proceedings, XXV. 197.

The second general method used in the preparation of baric bromide was based upon the decomposition of baric bromate. This salt was obtained in a very pure state by repeated recrystallization of the bromate remaining from the first preparation of hydrobromic acid by the method described above. In the course of the recrystallization it was noted that the glittering hard crystals emit brilliant flashes of bluish light upon being rubbed between the surfaces of moistened glass apparatus. This phenomenon takes place when there is no conceivable trace of organic matter present, and may be noticed even in the daylight. The substance was gradually raised to a dull red heat by means of a Berzelius lamp, no emission of light being noticed during its decomposition. The resultant baric bromide was dissolved, filtered, crystallized twice, washed with alcohol, and dried. After fusion over the spirit lamp the substance was redissolved, filtered, acidified with hydrobromic acid, and finally crystallized twice from water. Each yield of crystals was washed four times with the purest alcohol. In the first mother liquor a notable trace of sodium was found by the usual spectroscopic treatment, but no trace of calcium or strontium. The purest crystals were divided by yet another crystallization into three fractions, which we may call II.a, II.b, and II.c. The last was obtained by the evaporation of all the mother liquor decanted from the first two.

The third method used for the preparation of baric bromide adopted baric nitrate as its starting point. This salt, which had been recrystallized ten times, was dissolved in hot water and treated with the calculated amount of the purest obtainable potassic hydrate in a platinum bottle. The resulting baric hydrate was recrystallized ten times from hot water, without being removed from the bottle; but the spectroscope still showed noticeable traces of potassium upon the usual fractional treatment. The hydroxide was then precipitated three times successively from aqueous solution by means of pure alcohol, the precipitate being washed each time with alcohol, with the aid of the filter pump. Even the second mother liquor showed no trace of potassium to the most careful scrutiny.

The pure baric hydrate thus prepared was dissolved in pure water in the platinum bottle, boiled for some time to drive off the alcohol, transferred to a Bohemian flask, and saturated with pure bromine. This substance had been prepared as described on page 17, with the additional treatment of solution in pure calcic bromide and several distillations. The mixture of baric bromide and bromate was evaporated, powdered, and gradually raised to fusion in a platinum vessel. The mass was gray before fusion and pale green afterwards. The greenish cake was dissolved in water, filtered, acidified, crystallized, dried and fused; and then this same round of operations was again repeated. The last pure white cake of baric bromide was dissolved, the solution filtered, and after being very faintly acidified with hydrobromic acid was again crystallized. The final crystals were washed four times with alcohol, and allowed to dry in the air. In the table below (page 27) they are designated No. III. (Analyses 10, 11).

Since baric hydroxide is so easily recrystallized it was hoped that a pure preparation might be obtained directly in this way from the baryta of commerce. It has been already said that five recrystallizations remove the chlorine; five more remove the last traces of calcium. When, however, after seventeen recrystallizations, the large amount of strontium present did not seem to be considerably diminished, this method was abandoned as a hopeless one.

A long series of qualitative and quantitative experiments upon the fractional precipitation of baric carbonate by the action of small amounts of carbon dioxide upon baryta water showed that this process also was utterly unfitted for the complete separation of strontium from barium, and accordingly this method was abandoned. The description and data of these experiments would require much room, and, since the work was not fruitful, they may well be omitted.

Because of all these unsatisfactory results the baric hydrate was converted directly into baric bromide and bromate by the addition of pure bromine similar to that used in the preparation of Sample III. The large amount of bromide filtered off from the bromate was half crystallized out by boiling down the mother liquor in a platinum dish, treating with alcohol, and cooling. The mother liquor from these crystals contained most of the strontium. The solid was dissolved, boiled down, treated with alcohol and cooled; and the new crystals were washed four times with alcohol. After repeating this round of operations once again, the mother liquor showed no trace of strontium.* The pure crystals yielded a faintly brownish mass upon fusion, and this in turn left a brownish precipitate upon solution. The clear filtered liquid was boiled down and treated with alcohol just as described above. The crystals were again fused, and again subjected to the same succession of operations. For the last time the crystals were raised to a dull red heat by means of a spirit lamp, and the residue was dissolved in the purest water in a platinum dish, allowed to stand exposed to the air until neutral, filtered, recrystallized twice more, and washed with the purest alcohol. The resulting material was designated IV.a (Analyses 13, 14, 15). The last mother liquors were evaporated, and yielded IV.b (Analysis 12). Only about fifteen grammes of such pure material were obtained from a kilogramme of the baric hydroxide which served as the starting point. The earlier mother liquors containing strontium were used for the preparation of pure hydrobromic acid.

The fifth method for the preparation of baric bromide was the most complicated of all. A large amount of a solution of baric chloride ("purissimum") was allowed to stand for eighteen hours after the addition of a little pure baric hydrate and carbonate. To the filtered and slightly acidified liquid was added enough potassic chromate to precipitate about half the barium, the potassic chromate having been previously purified by continued shaking with a little baric chloride and hydrochloric acid, and by subsequent filtration. The large mass of baric chromate was washed by decantation with much water until no chlorine was to be found in the filtrate, and was almost wholly decomposed by strong nitric acid. The solution was diluted and shaken with the excess of baric chromate for a long time. Upon the neutralization of the nitric acid in the clear yellow filtrate with pure sodic carbonate, the baric chromate was largely recovered, and after a thorough washing it was again dissolved in nitric acid, and the baric nitrate was repeatedly crystallized until it was wholly colorless and neutral. By means of gradually increasing heat baric oxide was formed from this nitrate, the ignition taking place in a platinum crucible, and continuing until long after the frothing had ceased. The crucible itself lost several milligrammes during the process. The brownish residue was dissolved in water, and the clear colorless liquid was filtered from the brown precipitate. The baric hydroxide was neutralized with pure hydrobromic acid,* and the baric bromide was passed many times through the often repeated round of fusion, solution, filtration, and crystallization, until the fused cake was perfectly clear and colorless. After being faintly acidified with hydrobromic acid, the pure salt was crystallized, washed, and dried as usual. This specimen, which had been growing smaller and smaller in amount during the manifold processes to which it had been subjected, was enough only for one analysis (No. 16) and was designated V.

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* This method of freeing baric from strontic bromide suggests P. E. Browning's work with amyl alcohol, published since the experiment recorded above was completed. (Am. Journ. Sci., [3.] XLIV. 459.)

Out of the baric bromate which remained from the fourth preparation two other specimens of baric bromide were prepared. The only point in which this preparation differed from the second method was the fact of the strong acidification of the bromide with hydrobromic acid just before the final series of crystallizations. The crystallization was then continued until the mother liquors proved to be absolutely neutral. The purest crystals were designated VI.a; the mother liquor from them yielded VI.b (Analyses 17,18, 19).

It seemed probable that, if all these preparations gave about the same value for the molecular weight of baric bromide, they would fix this constant with comparative certainty. It is doubtful if the substance can be prepared in a state of absolute purity. Stas found it impossible to prepare any of his haloid salts in such a state,† a small amount of silica always remaining. The attempt was made to eliminate the silica from the preparations described above by repeated ignition and fusion, and the exclusive use of platinum vessels; but it cannot be proved that the attempt was wholly successful. However, the salt was at least as pure as our usual standards of reference.

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* This acid was from the same sample as that employed in making specimens I.b and I.c.

† See Stas's "Untersuchungen," Aronstein, pp. 269, 279, 346.

Silver. — Pure silver was prepared in the first place by the reduction of pure argentic chloride by pure milk sugar, after the well known method recommended by Stas. A full description of the details is to be found in the account of the analysis of cupric bromide;* indeed, some of the silver used in the present work was a portion of one of the large buttons made in 1890. Only in one particular was the mode of preparation modified: the silver was not heated with fused potassic hydroxide. Two or three buttons of the silver were fused with borax and sodic carbonate on hard-wood charcoal; this treatment made no essential change in its quantitative relations. The silver contained no oxygen, and gave very qualitative and quantitative evidence of purity.†

All of the silver which has been thus far described was fused in the flame of ordinary illuminating gas. Since a strongly reducing flame was used, it was presumed that no silver sulphide was formed. Nevertheless, it was deemed advisable to prepare a sample of the metal which should be free from even the possibility of reproach. Ordinary hydrogen is apt to be quite as impure as illuminating gas, hence as little adapted for the present purpose. For this reason, pure hydrogen was made from pure hydrochloric acid by the action of zinc which was quite free from arsenic. The gas was driven through water, much potassic hydrate, through a tube containing beads moistened with argentic nitrate, and finally through potassic permanganate, into a gas-holder over water, where it remained for some time. It was burnt in an oxyhydrogen blowpipe provided with a complete platinum tip, and served for the fusion of the silver used in Experiment 19. For the support of the metal during its fusion a cupel of sugar charcoal had been made from pure sugar by the sole use of an alcohol lamp as the source of heat. The silver itself was made from the pure silver first described by dissolving it in nitric acid and electrolytically depositing it with the aid of two Bunsen cells,‡ two plates of the same metal serving as electrodes. This method for the preparation of pure silver is a very satisfactory one. Since the silver was allowed to cool in an atmosphere of hydrogen, it could have contained no oxygen. The agreement of Experiment 19 with the others is satisfactory proof that the amount of sulphur contained in the first samples of silver must have been infinitesimal, if appreciable at all.

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* These Proceedings, XXV. 197, 198.

† Ibid.; also this paper, pages 17, 28, 29.

‡ J. L. Hoskyns Abrahall, Journ. Ch. Soc. Proc., 1892, p. 660.

Other Materials. — The methods used for the preparation of pure water, pure nitric and sulphuric acids, and pure sodic carbonate, have been discussed at length in a previous paper.* Precautions taken with regard to carbon dioxide, hydrobromic acid, and many other substances, are to be found under earlier heads. Alcohol was purified for the present investigation by repeated distillation in apparatus wholly free from cork or rubber connections. In some cases a platinum still was used.

The large mass of platinum used in the first experiments was kindly loaned by Professor Cooke, but subsequently a quantity was purchased especially for the work. The methods used in freeing the surface of these vessels from iron are described in the fourth paper upon the revision of the atomic weight of copper.†

THE METHOD OF ANALYSIS.

Thus far it has been found possible to determine accurately only the ratio of baric bromide to silver and argentic bromide. Unfortunately no accurate method for the direct determination of the amount of metal present is known to exist; hence a complete analysis is impossible.

The usual scheme of operations was very simple. The baric bromide, after having been pulverized in an agate mortar, was heated for a long time at 200–400°; it was then gradually raised to dull redness, and maintained for some time at that temperature. Repeated heating sometimes caused a very slight loss, due to increased decomposition; but more usually the weight remained constant. The drying oven was a large porcelain crucible, and at first illuminating gas was used as the source of heat. Afterwards, when a faint trace of cloudiness found in the solution of the baric bromide was traced to the formation of baric sulphate from the sulphur in the illuminating gas, an alcohol lamp was used exclusively. In Analyses 3, 4, 15, 16, and 17 the amount of this insoluble residue was determined, and appropriate correction was made. In

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* These Proceedings, XXVI. 245–249.

† Ibid., 249.

Analyses 6, 7, 9, and 12 the cloudiness of the solution was so slight as to be inessential, while in Analyses 2, 5, 8, 10, 11, 14, 18, and 19 the neutral solution of the baric bromide was absolutely clear.

The method of weighing was precisely similar to that employed with anhydrous cupric sulphate.* Afterwards the salt was dissolved in the purest boiled water, and the traces of baric hydrate and carbonate present were determined in the manner which has been already described.† The appropriate correction having been applied to the last weight of the baric bromide, the solution was diluted and transferred to a glass-stoppered Erlenmeyer flask. To this was added about the corresponding amount of accurately weighed silver, which had been dissolved in the purest nitric acid with all possible precautions.‡ The argentic nitrate solution had been freed from the lower oxides of nitrogen by long heating at 100° in an inclined flask, and both solutions were quite cold at the moment of precipitation. Daylight was carefully excluded during this operation, as well as during the subsequent ones. After violent shaking, the precipitate was allowed to settle, and the excess of bromine or silver was determined by titration. It is well known that even here there is a slight difference between the end points, although the possible error is very much less than with the chloride. In the table below the mean between the two extremes is recorded; and in general the observations and method of treatment corresponded essentially with those since published for the late J. L. Hoskyns Abrahall in the account of his interesting work on the atomic weight of boron,§ to which the reader is referred. The end point was always determined by titrating backward and forward until there could be no doubt of its accuracy, a cubic centimetre of each of the solutions employed corresponding to one milligramme of silver. In the final experiments the solutions were weighed as well as measured. For these experiments, a dark room was built, and provided with an arrangement, essentially similar to that described by Stas,‖ for condensing a beam of yellow light upon the surface of the liquid in the flask, leaving the precipitate in darkness.

In some cases the baric bromide was poured into the argentic nitrate,[*] instead of *vice versa*. This difference of procedure seemed to increase the distance between the two end points, but not to influence the final averaged result.[†]

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* These Proceedings, XXVI. 243, 252.

† This paper, page 12.

‡ These Proceedings, XXV. 198.

§ Edited by T. Ewan and P. J. Hartog, J. Chem. Soc. Proc., 1892, p. 663.

‖ Aronstein's translation, page 45.

In most cases a slight excess of hydrobromic acid was added before filtering, but the amount recorded in the table always represents that which was equivalent to the end point of the reaction. In Experiments 3, 6, 12, 14, and 15, where argentic nitrate was added in excess before filtration, the total amount of silver given in the table signifies the sum of the amount of silver weighed out and that which was added to attain the end point. The extra silver is of course not counted. The agreement of Analyses 14 and 15 with 18 and 19 is sufficient to show the accuracy of both methods. The clear yellow precipitate was washed by decantation until the filtrate became wholly neutral, and was collected and weighed on a Gooch crucible. The first filtrates were always passed through the crucible several times, for fear that a trace of asbestos might have been carried away. One of the absolutely clear filtrates containing a trace of hydrobromic acid gave no sign of a reaction for silver after evaporation to small bulk.

In a number of experiments, modifications in the methods described above were introduced. The most important change was the one adopted in Analyses 2, 8, 14, and 18. In these four cases the baric bromide was not heated at all, but the crystallized salt was dissolved directly in water.[‡] In order to determine the amount of anhydrous salt which must have been present in these specimens, parallel determinations of the water of crystallization were made with the greatest care upon precisely similar samples. The agreement of these results with the others is the best possible proof of the accuracy of the alkalimetric correction applied to those determinations in which the substance had been ignited.

In Experiments 4 and 13 the baric bromide was fused. In Analyses 6, 14, 15, 18, and 19 the argentic bromide was fused, and the weight of the fused salt is recorded in the final table. In the first case the substance had been slightly darkened by exposure to light; hence a little pure bromine vapor was added to the glass tube in which the fusion was conducted, and the bromide gained 0.07 milligramme during the process. The other results are tabulated below.

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[*] E. g. Exp. 14, 15, 16.

[†] Compare Stas, Mém. Acad. Belg., XLIII., Introduction.

[‡] This procedure was suggested by a part of Marignac's work on the chloride (*loc. cit.*).

No. of Analysis.	Weight of Argentic Bromide before Fusion.	Loss of Argentic Bromide on Fusion.
	Grammes.	Grammes.
14	7.17411	0.00018
15	4.4583	0.00001
18	3.63751	0.00013
19	4.37867	0.00000

In Experiment 11 a hard glass tube with small rubber stoppers was employed for the ignition of the baric bromide, but it was attacked by the salt and gained 0.10 milligramme during the heating. This gain corresponds to a loss of about the same weight of bromine, assuming all the barium which combined with the glass to have been converted to the oxide. For this reason the amount of hydrobromic acid recorded in the seventh column of the final table is about 0.12 cubic centimetre too large. In calculating the corrected weights of baric bromide, silver, and argentic bromide, allowance is made for all these facts. Because of the complication of all these little corrections, the glass tube was abandoned, and the platinum crucible was again used.

Data and Results.

The first column of the final Table of Data gives the number of the experiment. The second column contains the weight of the crystallized baric bromide, while the third contains the observed weight of the ignited baric bromide. After this is recorded the number of cubic centimetres of standard hydrobromic acid (of which one litre corresponded to a gramme of silver) required to restore the small amount of bromine lost during ignition. This quantity is divided into two parts, the upper one corresponding to baric hydroxide, and the lower to baric carbonate. Multiplying the upper figure in this column by $\frac{63}{108}$ milligramme, and the lower figure by $\frac{50}{108}$ milligramme, and adding the two products to the weight given in column III., we obtain the corrected weight of the baric bromide which is recorded in the fifth column. The sixth column gives the total weight of silver taken; the seventh, the number of cubic centimetres of the same hydrobromic acid necessary to titrate back to the mean end point; and the eighth, the weight

TABLE OF DATA. — ALL WEIGHTS ARE CORRECTED TO THE VACUUM STANDARD.

I. Number of Analysis.	II. Weight of Crystallized Baric Bromide.	III. Observed Weight of Anhydrous Baric Bromide.	IV. HBr Solution to Neutral Alkali.	V. Corrected Weight of Anhydrous Baric Bromide.	VI. Total Weight of Silver.	VII. HBr Solution to titrate back.	VIII. Weight of Silver corresponding to $BaBr_2$.	IX. Total Weight of Argentic Bromide.	X. Argentic Bromide corresponding to $BaBr_2$.	XI. Sample of Baric Bromide used.
	Grammes.	Grammes.	Cm.^{3}	Grammes.	Grammes.	Cm.^{3}	Grammes.	Grammes.	Grammes.	
1	2 56714	2.28760	....	....	1.66314	2.40	1.66074	2 89444	2.89026	I.a
2	3.89534	Not ignited.	0	3.4712	2.52554	5.35	2.52019	4.39566	4.38635	I.a
3	....	3.80860 *	1.90 2.50	3.81086	....	0.30	....	4.81740	4.81688	I.b
4	....	2.19830 *	1.65 0.25	2.1994	1.59832	1.45	1.59687	....	....	I.b
5	....	2.35954	0.12 0.22	2.35971	1.71613	2.90	1.71323	2.98735	2.98230	I.c
6	3.30433	2.94178	0.32 0.22	2.94207	2.13889	3.05	2.13584	3.72340	3.71809	II.a
7	1.80930	1.61177	0.16 0.11	1.61191	1.17100	0.80	1.17020	....	....	II.b
8	2.36427	Not ignited.	0.00	2.10633	1.53056	1.35	1.52921	2.66426	2.66191	II.b
9	....	2.91650	0.32 0.26	2.91682	2.11840	1.00	2.11740	3.68789	3.68615	II.c
10	2.66363	2.37226	0.38 0.90	2.37290	1.72298	0.22	1.72276	2.99906	2.99868	III.
11	2.07483	1.84804	0.14 0.00	1.84822†	1.34328	1.65 †	1.34175†	2.33797	2.33530†	III.
12	....	1.9038	1.40 0.00	1.9046	....	0.37	....	2.40798	2 40733	IV.b
13	2.75591	2.45417	3.06 0.30	2.45611	....	....	....	....	....	IV.a
14	6.35791	Not ignited.	0.00	5.66647	4.12090	7.30	4.11360	7.1739	7.1612	IV.a
15	3.95705 *	3.52610 *	0.35 0.85	3.5267	2.56100	0.90	2.56010	4.4583	4.4567	IV.a
16	4.8442 *	4.3161 *	0.00 1.75	4.3169	3.13550	1.20	3.13430	....	....	V.
17	3.78040 *	3.36557 *	0.15 1.50	3.36635	2.44567	1.82	2.44385	....	...	VI.b
18	3.22971	Not ignited.	0.00	2.87743	....	0.54	....	3.63738	3.63644	VI.a
19	3.88750	3.46330	0.03 0.32	3.46347	2.51529	1.14	2.51415	4.37867	4.37669	VI.a

* Corrected for small amount of baric sulphate (or silica) found on solution. † See page 26.

N. B. — Two weights (the argentic bromide of Analysis 4 and the silver of Analysis 18) are omitted from this table, as they were known to be in error. It might have been well to omit the whole of the twelfth experiment for the same reason. The other blanks were never filled.

of the silver corrected by subtracting from the weight given in column VI. the amount of silver corresponding to the quantity of acid given in column VII. In the same way, the ninth and tenth columns contain respectively the total and the corrected weight of argentic bromide. Hence the weights actually used in the calculation of the results are those recorded in columns V., VIII., and X.

The discussion of the results is simplified by reducing all the amounts of baric bromide to the basis of 100.000 parts of silver, and the corresponding quantity, 174.080 parts, of argentic bromide. The water of crystallization is included in the following table only because the calculation of Analyses 2, 8, 14, and 18 depends upon the knowledge of its amount. The great variations noticeable in the results for the water of crystallization are due to the varying circumstances attendant upon the crystallization, to the fineness of the powder, and to the hygroscopic condition of the air at the time of weighing the crystals. Hence for the present purpose it was possible to compare only like samples which had been weighed out under like conditions. Analyses 13 and 15 show that in this way perfect constancy can be reached. This part of the work has of course no other bearing upon the atomic weight of barium.

The first two experiments were merely preliminary, and are not included in the final average. Most of the variations evident in the earlier experiments were undoubtedly due to unfavorable conditions existing in the Laboratory during the year 1891–92. In the autumn of the latter year the Laboratory was completely and most admirably remodelled, through the kindness of the Corporation of the University, and the last seven experiments were performed under conditions as favorable as could be desired.

The presence of any of the most likely metallic impurities — strontium, calcium, potassium, or sodium — would tend to lower the observed values recorded in the third and fourth columns of the Table of Results, and hence the atomic weight of barium. Chlorine would lower and iodine would raise the values given in the third column, but neither would have much effect on those given in the fourth column. The best possible proof of the freedom of the preparations from these two impurities, as well as of the purity of the silver, is to be found in the series of results giving the per cent of silver in silver bromide, tabulated in the fifth column of the Table of Results.* The presence of water in the ignited baric bromide would naturally tend to raise the figures given in both the third

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* See also these Proceedings, XXV. 212.

TABLE OF RESULTS.

Number of Analysis.	Salt employed.	Parts of Baric Bromide corresponding to 100.000 Parts Silver.	Parts of Baric Bromide corresponding to 174.080 Parts Argentic Bromide.	Per Cent of Silver in AgBr.	Water of Crystallization in Baric Bromide.
1	I a	137.746	137.783	57.460	10.889
2	I.a	137.736	137.760	57.455	
3	I.b		137.723		
4	I.b	137.732			
5	I.c	137.735	137.739	57.447	
6	II.a	137.748	137.748	57.445	10.964
7	II.b	137.747			10.910
8	II.b	137.740	137.747	57.448	
9	II.c	137.755	137.748	57.442	
10	III.	137.738	137.752	57.451	10.915
11	III.	137.747	137.772	57.455	10.922
12	IV.b		137.726		
13	IV.a				10.878
14	IV.a	137.750	137.745	57.443	
15	IV.a	137.756	137.754	57.445	10.875
16	V.	137.731			10.885
17	VI.b	137.748			10.953
18	VI.a		137.745		
19	VI.a	137.759	137.758	57.445	
Aver., omitting Exp. 1 and 2.		137.745	137.747	57.448	
Average of last seven Exp.		137.749	137.751	57.444	
Stas found				57.445	

and fourth columns: the arguments indicating the absence of this insidious impurity were discussed at length in the first part of the paper.*

The agreement between the individual results is as close as could reasonably be expected, when one considers the small amounts of material used in some cases. It may be concluded, then, that a hundred parts of silver correspond to about 137.747 parts of anhydrous baric bromide, no matter what may be the method used for its preparation. If the salt contains an impurity, it is strangely constant in amount.

THE ATOMIC WEIGHT OF BARIUM.

From the results which have just been given, the atomic weight of barium is very readily computed. In the following table are given the values corresponding to the three standards at present in use.

From the Ratio of Silver to Baric Bromide.

If Silver = 107.93, and Bromine = 79.955, Barium = **137.426**
If Silver = 107.66, and Bromine = 79.755, Barium = 137.083
If Silver = 107.12, (Oxygen = 15.88,) Barium = 136.396

Greatest variations from the mean, $\left\{\begin{array}{l}+\ 0.030.\\-\ 0.040.\end{array}\right.$

From the Ratio of Argentic Bromide to Baric Bromide.

If Argentic Bromide = 187.885, Barium = **137.431**
If Argentic Bromide = 187.415, Barium = 137.089
If Argentic Bromide = 186.476, Barium = 136.401
Greatest variation from the mean, ±0.054.

It is not very difficult to explain the reason for the difference between this new value, 137.43, and the old one, 137.10. The incomplete knowledge regarding the end point of chlorine reaction in 1858 is probably responsible for a part of the difference, and a portion more may possibly be explained by the impurities which were assumed to be inessential. But it has already been said that a discussion of the results of thirty-five years ago can be of little value. The only true solution of the question is the experimental one. In the near future, I hope to continue the investigation which is herewith commenced, as well as to begin a similar research upon strontium and calcium.

CAMBRIDGE, December 24, 1892.

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* This paper, page 12.